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Synthesis and Fluorescent Properties of Oxime Ethers of 3-Acyl-1,2-dihydrocinnoline-N-phenyl-1,2-dicarboximide

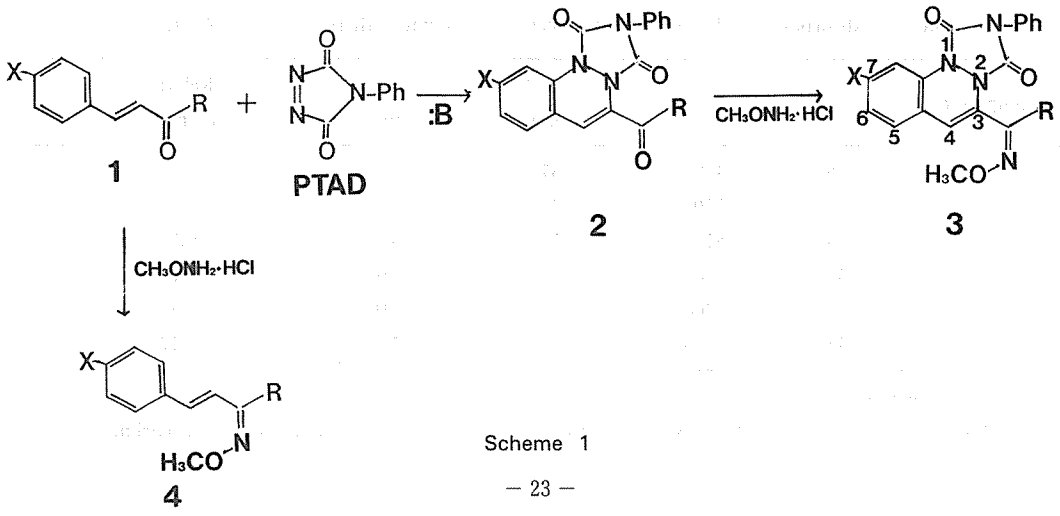
Satoko Tanaka and Kazuyoshi Seguchi
Department of Textiles and Clothing Sciences, Faculty of Home Economics, Mukogawa Women's University, Nishinomiya 663, Japan

Entitled oxime ethers containing N-phenyl-diazadicarboximide were synthesized from cycloadducts (keto-urazoles) obtained by the reaction of styryl ketones with PTAD. The oxime ethers showed fluorescence and a large Stokes shift. Based on the effects of solvents on their absorption and fluorescent bands, the structure of the excited state was discussed.

Introduction

The chemistry of urazole (1,2-diaza-1,2-dicarboximide) prepared from the cycloaddition of alkenes with 4-phenyl-4H-1,2,4-triazole-3,5-dione (PTAD) has been described mainly in connection with azo alkanes derived from hydrolysis of the urazoles.[1] The unique skeleton of urazole provides a new or an improved synthetic method of heterocycles as demonstrated in our previous report,[2] in which urazoles containing carbonyl group at the β-position to urazoyl group gave novel oxazolinones by the backbone-participated alcoholysis. In order to exploit further utility and synthetic application of urazoles, accumulation of chemical and physical data is to be wished. In the course of studying on backbone-participation concerning urazole, we synthesized oxime ethers 3 of keto-urazole 2. Interestingly, the pale yellow oxime ethers fluoresced from green to blue. This fluorescent phenomenum is the first example in the urazole chemistry as far as we know.

We will simply describe the fluorescent behavior of six oxime ethers based on the solvent effects in this paper.



Scheme 1

Results and Discussion

Synthesis of Oxime Ethers. The yellow keto-urazoles 2a-f containing carbonyl group at the β-position of urazoyl group were prepared from the addition-elimination reaction of styryl ketones 1a-f with PTAD.[3] The pale yellow oxime ethers 3a-f were synthesized by O-methyl oximation of the keto-urazoles 2a-f with O-methyl hydroxylamine hydrochloride in moderate yields according to the conventional method (Table 1).[4] The structures were determined by the ^1H NMR and the ^{13}C NMR spectroscopy. The mass spectra and IR spectra also supported the structures (see experimental section).

Fluorescence of Oxime Ether of Keto-Urazole. The synthesized oxime ethers 3a-f fluoresced from blue to green in the solid states and the acetonitrile solutions. Neither keto-urazole 2 nor oxime ether 4 of styryl ketones 1 showed fluorescence. Fluorescent behavior of a series of oxime ethers 3a-f was investigated by use of a fluorescent spectrophotometer. The results were presented in Table 2 together with the data of the absorption spectra. As compared with 3a and 3b (or 3d and 3e), the electron-releasing substituent at 7-position showed no effect on λ_{max} and F_{max} and rather caused the lowering of the fluorescent intensity (Table 2). However, the phenyl group (3d and 3c) or the styryl group (3f) conjugated with the oxime group caused the shift of the fluorescent maximum to longer wave length. The values of ε_{max} suggest $\pi \rightarrow \pi^*$ excitation of the double bond of carbon and nitrogen in oxime.

Taking into account that 2 and 4 showed no fluorescence and no example has been reported so far concerning fluorescence of urazoles, these fluorescence observed in the oxime ethers of keto-urazoles should be attributed to interaction between the urazoyl group and the oxime ether group in the excited state. we estimated intramolecular charge-transfer compounds in the excited state such as Ⅰ and Ⅱ.

Effect of Solvent on Fluorescence of 3a. In order to elucidate the structure of the excited state, the solvent effects on the absorption and the fluorescent spectra of 3a were investigated using fourteen solvents. The observed absorption maxima (λ_{max}), the molecular absorption coefficients (ε_{max}), the fluorescence maxima (F_{max}), and the fluorescent intensity were listed in Table 3 and herein Stokes shift (SS) means the difference between the

Table 1. Yields of Oximation

	X	R	Yield (%)[a]
3a	H	Me	53
3b	OMe	Me	42
3c	H	Et	35
3d	H	Ph	80
3e	OMe	Ph	42
3f	H	CH=CH−Ph	25

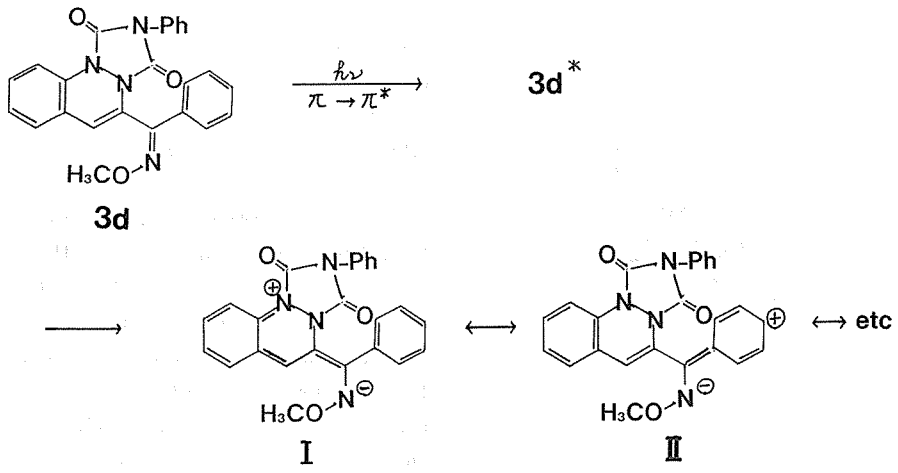
a) Based on **2**.

Table 2. Absorption and Fluorescent Spectra of Oxime Ethers **3a−f** in Acetonitrile

Compound	λ_{max} (nm)	ε_{max}	E_{max}[a] (nm)	F_{max} (nm)	Relative Intensity[b]
3a	365	4200	372	494	1.00
3b	365	7200	370	488	0.02
3c	364	5200	372	497	0.76
3d	367	3700	378	510	0.23
3e	364	6200	380	510	0.11
3f	364	4300	370	510	0.22

a) Wave−length of excitation.

b) Values relative to **3a**. Fluorescent intensity of **3a** is 0.062 as compared with carbazole.



Scheme 2

Table 3. Absorption and Fluorescent Spectra of Oxime Ether **3a** in Various Solvents

No.	Solvent	E_T[a]	λ_{max} (nm)	F_{max} (nm)	Relative Intensity[b]	SS[c] (nm)
1	MeOH	55.5	360	510	0.06	150
2	EtOH	51.9	361	506	0.12	145
3	1-BuOH	50.2	363	508	0.16	145
4	2-PrOH	48.6	357	500	0.18	143
5	Acetonitrile	46.0	365	494	1.00	129
6	DMSO	45.0	372	508	0.76	136
7	DMF	43.8	370	506	0.30	136
8	Acetone	42.2	366	502	0.44	136
9	Chloroform	39.1	362	490	0.93	128
10	Ethyl acetate	38.1	369	500	0.53	131
11	THF	37.4	369	500	0.53	131
12	1,4-Dioxane	36.0	370	496	0.79	126
13	Benzene	34.5	371	490	1.07	119
14	CCl_4	32.5	370	490	0.35	120

a) Senoo M. and Arai T., "Yobai-kouka", Sangyo-tosho(1970), p.69.
b) See Table 2. c) Stokes shift.

fluorescent maxima and the absorption maxima. The observed Stokes shift reached to unusual value as high as 150 nm and can be explained from solvent effects taking to excitation[5]. The values of Stokes shift were plotted against the polarity parameters of the solvents, E_T in Fig.1. The fact that the relationship gave a straight line approximately, indicates that the excited state is more polar than the ground state. The contribution of intramolecular charge separation to the excited state such as I and II etc. may be responsible for the large Stokes shift and the corelationship in Fig.1. The fluorescent intensity was weaker in protic solvents than in aprotic solvents as seen in Table 3. These facts also suggest that hydrogen-bonded solvation due to protic solvents toward the charge separated species in the excited state occurs, and deactivates the excited state more efficiently.

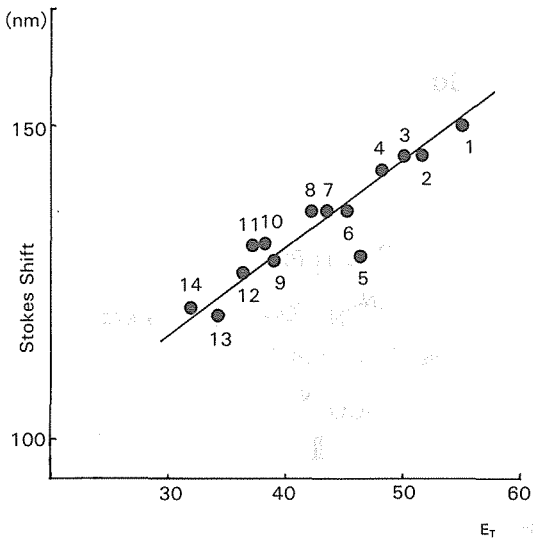


Fig. 1. Relation between Stokes shift and E_T. Numerals denote solvents in Table 3.

In conclusion, the oxime ethers conjugated with the urazoyl group are new organic fluorescent compounds. The further syntheses and the applications of the derivatives are now in progress.

Experimentals

Instruments and Materials. Melting points were determined on a Shimadzu MM-2 apparatus. NMR spectra were obtained with a JEOL FX 200 and a Hitachi R-600 spectrometers in a $CDCl_3$ solution, using tetramethylsilane as an internal standard. IR spectra were recorded on a Shimadzu R-460 spectrometer. Mass spectra were measured by a JEOL JMS DX-303 spectrometer. The guaranteed grade solvents were used without further purifications. According to the previous report,[3] 3-Acyl-1,2-dihydrocinnoline-N-phenyl-1,2-dicarboximide 2a-f were prepared by the addition-elimination reaction of styryl ketones with PTAD.

General Synthesis of oxime ether 3. To 313mg(0.90 mmol)of 2a in 30ml of ethanol was added 114mg(1.40 mmol) of O-methyl hydroxylamine hydrochloride and the mixture was refluxed for 12hr with checking disappearance of the starting material by TLC. For 2c were adopted the reaction conditions of 7 days at 100°C in the autoclave (Taiatu glass Co.). After cooling, the precipitation was filtered by suction, and recrystallized from ethanol. Similar procedures were performed for 2b and 2d-f. The resulting pale yellow solid was obtained in 25-80% yields(See Table 1).

3a; mp 197-198°C; ^{1}H NMR δ=2.09(s, 3H, Me), 3.96(s, 3H, OMe), 5.85(s, 1H, 4-H), and 6.93-7.53(m, 9H, Ph); ^{13}C NMR δ=15.6(q, Me), 62.3(q, OMe), 110.1(d), 115.1(d), 120.8(s), 125.7(d), 126.9(d), 128.6(d), 129.2(d), 129.7(d), 130.7(s), 130.9(s), 133.6(s), 143.2(s), 145.4(s), and 150.6(s); IR 1757, 1711, 1413, 1357, and 1052 cm^{-1}; MS m/z(%) 348(100, M$^+$), 317(16), 201(17), 17(23), and 130(28).

3b; mp 190-191°C; ^{1}H NMR δ=2.10(s, 3H, Me), 3.80(s, 3H, C-OMe), 3.95(s, 3H, N-OMe), 5.83(s, 1H, 4-H), and 6.57-7.93(m, 8H, Ph); IR 1750, 1706, 1418, 1361, 1048, and 1033 cm^{-1}; MS m/z(%) 378(100, M$^+$), 187(77), and 160(42).

3c; mp 101-102°C; ^{1}H NMR δ=1.10(t, 3H, CH_3), 2.60(q, 2H, CH_2), 3.93(s, 3H, OMe), 5.79(s, 1H, 4-H), and 6.87-7.47(m, 9H, Ph); IR 1761, 1717, 1407, 1357, and 1046 cm^{-1}; MS m/z(%) 362(100, M$^+$), 331(27), 184(55), and 157(76).

3d; mp 174-175°C; ^{1}H NMR δ=4.00(s, 3H, OMe), 6.07(s, 1H, 4-H), and 7.03-8.33(m, 14H, Ph); IR 1767, 1715, 1488, 1408, 1352, and 1041 cm^{-1}; MS m/z(%) 410(100, M$^+$), 262(57), and 157(47).

3e; mp 104-105°C; ^{1}H NMR δ=3.78(s, 3H, C-OMe), 3.97(s, 3H, N-OMe), 5.73(s, 1H, 4-H), and 6.83-8.00(m, 13H, Ph); IR 1765, 1710, 1500, 1412, and 1228 cm^{-1}; MS m/z(%) 440(91, M$^+$), 292(31), and 187(100).

3f; mp 213-214°C; ^{1}H NMR δ=4.00(s, 3H, OMe), 5.93(s, 1H, 4-H), and 6.90-7.57(m, 16H, CH=CH, Ph); IR 1750, 1713, 1414, 1356, and 1050 cm^{-1}; MS m/z(%) 436(100, M$^+$), 244(32), 157(35), and 129(31).

The General Procedure of Measurements of Fluorescence and Absorption Spectra of 3. The fluorescence spectra were recorded on a Hitachi

650-10S fluorescent spectrophotometer in a quartz cell. The absorption spectra were measured using a Shimadzu UV-265 spectrometer. 3 were dissolved in acetonitrile and the solution were adjusted at a concentration of 10^{-4}mol•dm^{-3}. Furthermore, these spectra were measured using fourteen solvents as shown in Table 3.

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